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(54) HYDROGEN STORAGE ALLOY EXCELLENT IN DURABILITY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogen storage alloy, suitable for hydrogen storage and transport, heat transport and cooling system, gaseous hydrogen purification, etc., having high hydrogen occluding capacity and long-term repeated hydrogen absorbing and releasing life (hardly causing pulverization), usable at temps. in the vicinity of room temp., excellent in oxidation resistance, and capable of handling with ease in the air, and its production.

SOLUTION: The hydrogen storage alloy, having a chemical composition represented by formula TiaV1-a-bCrb where the values of (a) and (b) are 0.3-0.5 and 0.1-0.45, respectively, and also having a structure in which the average crystalline grain size of the main phase is regulated to $40 μm, is produced by means of rapid solidification. The oxidation resistance of this hydrogen storage alloy can be remarkably improved by applying Ni coating to the surface of the alloy and then applying heat treatment at 400-750°C or by applying Ni coating to the surface of the alloy by means of mechanical alloying to form an Ni-addition layer composed essentially of Ti-Ni compound on the surface.

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* NOTICES *

CLAIMS

[Claim(s)]

[Claim 1] Tia V1-a-bCrb It is expressed with a formula and the value of a The value of 0.3-0.5b Hydrogen storing metal alloy which has the chemical composition which are 0.1-0.45, and is characterized by the diameter of average crystal grain of the main phase being 40 micrometers or less.

[Claim 2] The hydrogen storing metal alloy according to claim 1 which has nickel addition layer which makes a Ti-nickel compound a subject on a front face.

[Claim 3] Tia V1-a-bCrb It is expressed with a formula and the value of a The value of 0.3-0.5b The manufacture method of a hydrogen storing metal alloy according to claim 1 which consists of manufacturing the alloy which has the chemical composition which are 0.1-0.45 by the rapid solidification method.

[Claim 4] Tia V1-a-bCrb it expresses with a formula -- having -- value of a Value of 0.3-0.5b the alloy which has the chemical composition which are 0.1-0.45 -- a rapid solidification method -- manufacturing -- the front face of this hydrogen storing metal alloy -- nickel covering -- carrying out -- subsequently -- The manufacture method of a hydrogen storing metal alloy according to claim 2 which consists of heat-treating at the temperature of 400 - 750 **.

[Claim 5] Tia V1-a-bCrb It is expressed with a formula and the value of a The value of 0.3-0.5b The manufacture method of a hydrogen storing metal alloy according to claim 2 which manufactures the alloy which has the chemical composition which are 0.1-0.45 by the rapid solidification method, and consists of carrying out nickel covering of the front face of this hydrogen storing metal alloy by the mechanical alloying method.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention is the amount of hydrogen absorption. (hydrogen-absorption capacity) Highly and simultaneous, repeatedly, it is few, and property degradation by hydrogen absorption discharge can use at the temperature near the room temperature, and is related with a hydrogen storing metal alloy with the feature of being comparatively cheap, and its manufacture method. The hydrogen storing metal alloy of this invention with the above-mentioned feature is the the best for the object for hydrogen gas storage, and hydrogen gas refining.
[0002]
[Description of the Prior Art] Hydrogen gas is an energy source cleaner than the fossil fuel of the former [form / neither carbon dioxide gas nor nitrogen oxide / at the time of combustion]. Although the high-pressure hydrogen gas container was used in many cases on the occasion of its storage and transportation, since liquefaction temperature of hydrogen gas was low, it had to use the large-sized bomb for saving a lot of hydrogen gas, and had the fault that the storage container volume and weight became large.
[0003] As for a hydrogen storing metal alloy, since the absorption discharge of the hydrogen gas can be carried out in reversible, if the hydrogen storing metal alloy which can carry out occlusion of a lot of hydrogen gas is used for storage and transportation of hydrogen, since it will become more nearly lightweight than the bomb which can store a lot of hydrogen by high density, and stores the hydrogen of this capacity rather than a bomb, transportation also has easily the advantage that it is strong also against a mechanical shock. Therefore, research and development of the hydrogen storing metal alloy aiming at hydrogen storage and transportation have been done conventionally.
[0004] Since absorption of the hydrogen by the hydrogen storing metal alloy is the hydrogenation reaction of an alloy and discharge of hydrogen is the decomposition reaction of a hydride, at the time of absorption of hydrogen gas, and discharge, generation of heat and an endothermic are produced, respectively. This property is used and they are a heat-transport system, and warming or a cooling system about a hydrogen storing metal alloy. (an example, heat pump) Using is also possible.
[0005] The hydrogen absorption discharge speed of a hydrogen storing metal alloy is larger than the rate of absorption of other gas constituents, and since there is a difference also by hydrogen and its isotope, a hydrogen storing metal alloy can also be used for the use which refines hydrogen gas out of the gas containing impure gas constituents using the difference in such a hydrogen-absorption property.
[0006] For the above-mentioned use, a hydrogen storing metal alloy will all repeat and receive absorption and discharge of hydrogen gas while in use. In order to obtain a practical reaction rate in absorption and discharge of this hydrogen gas, it is necessary to powder-ize a hydrogen storing metal alloy and to increase a surface area. A predetermined container is filled up with this powdered hydrogen storing metal alloy, and use is presented.
[0007] In case a hydrogen storing metal alloy absorbs and emits hydrogen gas, in addition to the above-mentioned generation of heat and endothermic, expansion and contraction of about 10 - 20% of volume also take place. Therefore, if absorption and discharge of hydrogen gas are repeated and received while in use, a crack will go into the powder of a hydrogen storing metal alloy, and the pulverization which a powder particle is destroyed and becomes an impalpable powder will happen. If this pulverization advances, fines will be got blocked within a container and the problem that hydrogen gas will not flow easily or fines move into gas piping by the flow of hydrogen gas will arise. The pulverization suppression in the end of an alloy powder in repeat use poses a very big problem from such a situation in utilization of a hydrogen storing metal alloy.
[0008] An alloy cannot prevent touching with the atmosphere at the time of production of the hydrogen-absorption equipment using the hydrogen storing metal alloy. If a hydrogen storing metal alloy touches and oxidizes to the

atmosphere, since an oxide film will generate on an alloy front face and the oxide film will serve as an obstacle of hydrogen absorption, hydrogen storage capacity falls. Especially as for V alloy, it is tended to check oxidization hydrogen absorption. In order to enable it to use V alloy which oxidized at once, a hydrogen bomb which is equal to such processing is not only expensive, but it must heat a hydrogen storing metal alloy to an elevated temperature in high-pressure hydrogen, and size and weight increase are not avoided. Then, the oxidation-resistant improvement of a hydrogen storing metal alloy is also a practically important problem.
[0009] Thus, although there is a broad use in a hydrogen storing metal alloy, even when using for what use, the amount of hydrogen absorption is the most important property. Moreover, depending on a use, it is the comparatively low temperature near the room temperature. (an example and below 150 **) It is also important that absorption and discharge of hydrogen take place. Furthermore, the price of an alloy is also very important practically for the use which uses a hydrogen storing metal alloy in large quantities.
[0010] For example, LaNi5 which utilization preceded most Or MmNi5 AB5 represented It is expensive, and even if the amount of the hydrogen storing metal alloy used can use the hydrogen storing metal alloy of type for few small rechargeable batteries, it is difficult to use it for the use which needs a lot of hydrogen storing metal alloys called the object for hydrogen storage.
[0011] To JP,59-38293,B, it is comparatively cheap, and the Ti-Cr-V system hydrogen storing metal alloy is indicated as a high capacity hydrogen storing metal alloy. As the manufacture method of an alloy, only the arc process is explained concretely. The hydrogen storing metal alloy which consists of the same components also as JP,7-252560,A is indicated. The analogous hydrogen storing metal alloy of a Ti-V-nickel system is indicated by JP,7-268513,A and JP,7-268514,A.
[0012] Moreover, it is explained to JP,60-190570,A that influence of contamination by the impurity gas in atmosphere can be made small by covering copper and/or a nickel metal with wet electroless deposition to hydrogen storing metal alloy powder.
[0013]
[Problem(s) to be Solved by the Invention] It has been experienced that they are not right in fact although a theory top should have many amounts of hydrogen absorption and the Ti-Cr-V system hydrogen storing metal alloy and Ti-V-nickel system alloy which were mentioned above must be excellent in hydrogen-absorption capacity. This is considered that a cause is for 2nd phase called TiCr2 with few amounts of hydrogen absorption to generate, therefore for hydrogen-absorption capacity decline by such alloy system.
[0014] For example, when it manufactures by the arc process as indicated by this official report, since solidification speed is slow, a Ti-Cr-V system hydrogen storing metal alloy given in JP,59-38293,B is low TiCr2 of hydrogen storage capacity as the 2nd phase sludge. An intermetallic compound generates at a remarkable rate and hydrogen storage capacity declines. Moreover, a crack enters with this 2nd phase as the starting point into the repeat of hydrogen absorption and discharge in the end of an alloy powder, and there is also a trouble that pulverization is promoted.
[0015] In the example of JP,7-252560,A, in order to reduce the 2nd above-mentioned phase, after holding at the elevated temperature of 1200-1400 degrees C and considering as a cubic single phase organization, the process which quenches with water cooling immediately is taken. However, since big and rough-ization of crystal grain arises in the case of heating-at-high-temperature maintenance, even if the amount of sludges of the 2nd phase decreases, the intensity of the material itself becomes weak by big and rough-ization, and it on the contrary becomes easy to carry out pulverization of it by such method. In case it moreover mass-produces industrially, in order to use a large-sized ingot, even if it carries out water cooling after heating, sufficient cooling rate will not be obtained, but a big and rough sludge will be formed, and hydrogen storage capacity will also decline.
[0016] A Ti-nickel intermetallic compound is characterized by forming a 3-dimensional mesh frame at a grain boundary into the host phase which a Ti-V-nickel system hydrogen storing metal alloy given in each official report of JP,7-268513,A and said 268514 numbers becomes from a Ti-V system solid-solution alloy. Since such a grain-boundary phase raises reactivity with the hydrogen of an alloy, even if a mother layer has some oxidization, hydrogen gas absorption discharge is possible through this grain-boundary phase. However, since many 2nd phase to the extent that the 3-dimensional network structure is taken is formed, the hydrogen quantity to be stored of the whole alloy falls by the low 2nd phase formation of hydrogen-absorption capacity, and there is a trouble that the pulverization on the basis of this 2nd phase arises.
[0017] Moreover, since there is no hydrogen-absorption capacity in this covering itself when Cu or nickel metal is covered on the surface of a hydrogen storing metal alloy like a publication to JP,60-190570,A, only in the part of covering, the amount of hydrogen absorption will decrease.
[0018] Even if this invention has repeat hydrogen absorption / discharge life high hydrogen-absorption capacity

applicable to storage and transportation of hydrogen, a heat transport, a cooling system, hydrogen gas refining, etc., and over a long period of time, and it can be used for it at the temperature near the room temperature and it keeps it in the atmosphere, it makes a technical problem the thing with little hydrogen-absorption property degradation for which a comparatively cheap hydrogen storing metal alloy is offered.

[0019]

[Means for Solving the Problem] This invention persons have high hydrogen-absorption capacity and outstanding repeat hydrogen absorption / discharge life, and are low temperature (150 degrees C or less) near the room temperature comparatively. As a result of doing research on the hydrogen storing metal alloy which can be used, when the Ti-Cr-V system hydrogen storing metal alloy was manufactured by the rapid solidification method and the diameter of crystal grain was made small, it found out that the above-mentioned technical problem was solvable, and this invention was reached.

[0020] this invention is Tia V1-a-bCrb here. It is expressed with a formula and the value of a The value of 0.3-0.5b It is the hydrogen storing metal alloy which has the chemical composition which are 0.1-0.45, and is characterized by the diameter of average crystal grain of the main phase being 40 micrometers or less.

[0021] This hydrogen storing metal alloy is Tia V1-a-bCrb. It is expressed with a formula and the value of a The value of 0.3 to 0.5 and b It can manufacture by ingoting the alloy which has the chemical composition which are 0.1-0.45 by the rapid solidification method.

[0022] In the suitable mode of this invention, it has nickel addition layer to which a hydrogen storing metal alloy makes a Ti-nickel compound a subject on a front face. the front face of a hydrogen storing metal alloy which manufactured this nickel addition layer by ** rapid solidification method -- nickel covering -- carrying out -- subsequently -- or it heat-treats at the temperature of 400 - 750 ** -- or ** -- it can form by carrying out nickel covering of the front face of this hydrogen storing metal alloy by the mechanical alloying method

[0023]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. The feature of the hydrogen storing metal alloy of this invention is **Tia V1-a-bCrb. Chemical composition shown (the inside of a formula, a:0.3-0.5, b:0.1-0.45) The diameters of average crystal grain of the ** main phase are 40 micrometers or less and two points of being detailed.

[0024] The main phase of this hydrogen storing metal alloy is a dissolution body whorl which consists of three elements of Ti, V, and Cr, and a crystalline form is a body center cubic. The diameter of average crystal grain of the detailed main phase of the above-mentioned ** can attain a hydrogen storing metal alloy by manufacturing by rapid solidification methods, such as a chill roll method and the gas atomizing method. For example, if the cooling rate at the time of solidification becomes slow like an arc solution process, since crystal grain will grow and it will become big and rough during solidification, the diameter of average crystal grain of the main phase will exceed 40 micrometers.

[0025] The Ti-V-Cr system hydrogen storing metal alloy of this invention which fulfills the conditions of above ** and ** Low TiCr2 of hydrogen-absorption capacity Since there are few amounts of deposits of the 2nd said phase The temperature requirement below 150 ** is also 0.1 MPa near the atmospheric pressure. Absorbing very many hydrogen gas, the amount of hydrogen absorption is H/M. Ratio (a number of a hydrogen atom of ratios absorbed to one metal atom which constitutes an alloy) 1.5 It increases with the above. Moreover, 0.1 MPa It is endurance that use near the room temperature below 150 ** is possible, and it is hard to receive pulverization since the temperature which shows balanced hydrogen pressure is as low as below 150 **. (life) It becomes the hydrogen storing metal alloy which was very excellent. Moreover, since the rare earth metal is not included, the raw material cost of an alloy is not so high, either.

[0026] The crystalline form of the sludge of the 2nd above-mentioned phase is hexagonal or a cubic, and this exists in the interior of the grain-boundary section of a body center cubic which is the main phase of the hydrogen storing metal alloy of this invention, or a grain. First, the reason which limited the chemical composition of the hydrogen storing metal alloy of this invention like ** is explained. In addition, as shown in the formula of the above-mentioned chemical composition, each amount of each element is an atomic ratio, and the sum total is set to 1.

[0027] (Titanium Ti): If the amount of Ti increases, the grid size of the alloy main phase of a body center cubic will be expanded, and the amount of hydrogen absorption will increase. H/M 1.2 It is 0.3 in order to obtain the above high amount of hydrogen absorption. If the above Ti is required and the amount of Ti is less than this, the amount of hydrogen absorption will become low. If many titanium is added too much, although the amount of hydrogen absorption will increase further, hydrogen equilibrium pressure falls too much and it becomes impossible to use near a room temperature and the atmospheric pressure.

[0028] Therefore, although Cr is added as an element which raises hydrogen equilibrium pressure, the amount of Ti

is 0.5. Endurance over the pulverization by the repeat of hydrogen absorption and discharge when hydrogen equilibrium pressure cannot be raised to near the atmospheric pressure even if it adds Cr, if it exceeds (alloy life) It gets worse. addition of Ti from a viewpoint of balance with the amount of hydrogen absorption, and an alloy life the range of 0.3-0.45 -- desirable -- more -- desirable -- 0.3-0.4 It is within the limits.

[0029] Chromium (Cr): If Cr addition increases, although the amount of hydrogen absorption increases, it is not so large as titanium the extent. The key objective of Cr addition is in control of hydrogen equilibrium pressure. Therefore, the addition changes with the service temperatures and hydrogen equilibrium pressure which are made into Ti addition and the purpose. Cr is 0.1. In the case of Ti0.3, the hydrogen equilibrium pressure in a room temperature becomes below atmospheric pressure, and it is no longer made to absorb and emit hydrogen in reversible at a room temperature at the following. TiCr2 which deposits as the 2nd phase on the other hand if Cr exceeds 0.45 Not only the amount of hydrogen absorption falls, but the amount of a phase increases and the life over repeat hydrogen absorption and discharge falls. the addition of Cr -- from a viewpoint of the balance of the amount of hydrogen absorption, and an alloy life within the limits of 0.2-0.45 -- desirable -- more -- desirable -- 0.3-0.4 it is .

[0030] (Vanadium V): With the 2 yuan system alloy of Ti-Cr, it is TiCr2 as the 2nd phase. It forms mostly and the amount of hydrogen absorption and an alloy life fall, and since hydrogen equilibrium pressure is also too low and use at a room temperature is difficult for it, V is added. Many body center cubic phases are obtained by addition of V, and the amount of hydrogen absorption increases. The addition of V is automatically determined by the addition of Ti and Cr.

[0031] If the amount of hydrogen absorption of this alloy changes with the diameters of average crystal grain of the manufacture method or the main phase, the cooling rate at the time of solidification becomes slow and the diameter of average crystal grain of the main phase exceeds 40 micrometers even if it has the chemical composition of the Ti-Cr-V ternary system explained above, even if it is the same chemical composition, the amount of hydrogen absorption will fall. This is TiCr2 when solidification speed falls. Since this sludge has few amounts of hydrogen absorption of itself, when the rate in which a sludge [like] is formed as the 2nd phase increases, and the 2nd phase of the amount of formation increases, the amount of hydrogen absorption as the whole alloy is for falling.

[0032] If the rate in which this sludge is formed as the 2nd phase increases, since Ti in the alloy phase of a body center cubic which is the main phase, and the amount of Cr(s) will fall, it originates mainly in the amount reduction of Cr(s), the hydrogen equilibrium pressure which is balanced gas ** of hydrogen absorption and release reaction falls the amount of hydrogen absorption of the main phase not only decreases, but, and it becomes impossible moreover, to emit the hydrogen absorbed in reversible.

[0033] In addition, it also sets to the hydrogen storing metal alloy of this invention which fills both the above-mentioned ** and **, and is TiCr2. Although it is not avoided that a sludge [like] deposits as the 2nd phase, since there are few the amounts, these troubles are canceled substantially.

[0034] Furthermore, the hydrogen storing metal alloy of this invention is pulverization to which expansion and contraction of the alloy volume by the repeat of absorption and discharge of hydrogen take place owing to. (it can judge by the fall of a powder mean particle diameter) It is hard to receive and excels in endurance very much. This outstanding endurance is MmNi5 known as a rare earth system hydrogen storing metal alloy. It is more remarkably [than a system intermetallic compound] good.

[0035] However, if it changes with the diameters of average crystal grain of the manufacture method or the main phase, the cooling rate at the time of solidification becomes slow like [the endurance over this pulverization] the amount of hydrogen absorption and the diameter of average crystal grain of the main phase exceeds 40 micrometers, pulverization will become easy to happen even if it is the same chemical composition. TiCr2 which is the 2nd phase when a cooling rate becomes slow in this way, as mentioned above Since the amount of generation increases, pulverization is presumed that the intergranular fracture on the basis of this 2nd phase is the main factor.

[0036] From the above knowledge, the diameter of average crystal grain of the main phase is limited to 40 micrometers or less by the hydrogen storing metal alloy of this invention. Endurance over pulverization (alloy life) In order to improve further, it is desirable that the diameter of average crystal grain of the main phase is 20 micrometers. Moreover, it is hard coming to generate after ******** in 5 micrometers or less, and if the diameter of average crystal grain of the sludge formed as the 2nd phase is 2 micrometers or less, it will hardly carry out pulverization.

[0037] The hydrogen storing metal alloy of this invention whose diameter of average crystal grain of the main phase is 40 micrometers or less can be manufactured by ingoting the alloy molten metal of predetermined composition by the rapid solidification method. As long as the hydrogen storing metal alloy of this invention with the diameter of average crystal grain of the above [a rapid solidification method] is obtained, there is no limit.

Generally, a cooling rate is 103 **/sec. What is necessary is just the solidifying method which becomes the above.
[0038] As a rapid solidification method employable by this invention, it is the method of carrying out teeming of the alloy molten metal on a rotational electrode process, a rotating drum, or a roll. (an example, a single roll, or congruence chill roll method) A method, the gas atomizing method, etc. which are thinly cast to up to a water-cooled copper plate are mentioned. A rotational electrode process and the atomizing method have [among these] a powder configuration advantageous at the point that pack density becomes high in a globular form substantially, when the pulverization process for being able to manufacture the spherical-powder end of a hydrogen storing metal alloy, and powder-izing becomes unnecessary. In the case of other methods, the hydrogen storing metal alloy obtained if needed is ground, and it is made powder. As the pulverization method, both hydrogenation pulverization and machine pulverization can be adopted and both may be used together.
[0039] It is appropriate for the hydrogen storing metal alloy of this invention to consider as the powder form whose mean particle diameter is about 10-50 micrometers. Thereby, a surface area increases and absorption and release reaction of hydrogen are promoted. If required, a classification will adjust a mean particle diameter.
[0040] The hydrogen storing metal alloy of this invention manufactured by the rapid solidification method has a minute quenching distortion. This quenching distortion is the endurance of the hydrogen storing metal alloy of this invention. (pulverization) Although not generated, especially a remarkable bad influence may heat-treat a hydrogen storing metal alloy by request, and may remove this quenching distortion. As for this heat treatment, it is desirable to carry out in a vacuum or inert gas in order to prevent oxidization of an alloy.
[0041] It is necessary to set up heat treatment conditions so that there may be no bird clapper during heat treatment more greatly [the diameter of average crystal grain of the alloy main phase] than 40 micrometers. This condition is usually temperature, although it changes also with diameters of average crystal grain of the main phase of the hydrogen storing metal alloy manufactured by the rapid solidification method. It is within the limits of 400-750 degree-Cx 2 - 20 hours.
[0042] However, since it may heat-treat in the formation process of this layer and quenching distortion is also removed during this heat treatment when forming in an alloy front face nickel addition layer which makes a Ti-nickel compound a subject in order to raise the oxidation resistance of the hydrogen storing metal alloy of this invention so that it may mention later, heat treatment of only the purpose of removal of the quenching distortion in that case is unnecessary. It is not desirable from a viewpoint of big-and-rough-izing of the diameter of average crystal grain to perform two heat treatments to the hydrogen storing metal alloy of this invention.
[0043] The hydrogen storing metal alloy of this invention is the low temperature near a room temperature, when it is left in the atmosphere. (an example, 70 degrees C) The measured amount of hydrogen absorption decreases. This alloy that carried out air neglect is also among high-pressure hydrogen gas. (20 atmospheric pressure) If it is made to heat and reactivate to 500 **, the amount of hydrogen absorption will increase and the amount of absorption before neglect will be recovered. That is, if this alloy is left in the atmosphere, a front face will oxidize, and this oxide film is considered that it becomes an obstacle and the hydrogen storage capacity in low temperature decreases.
[0044] In order that it may not be avoided for the use of the object for storage or the object for refining of hydrogen gas that a hydrogen storing metal alloy is **(ed) by the atmosphere and operating temperature may avoid the fall of below 150 ** and the amount of hydrogen absorption by the above-mentioned oxidization since it is low temperature comparatively, it is desirable to improve the oxidation resistance of the hydrogen storing metal alloy of this invention.
[0045] As a result of examining this point, when the front face of the hydrogen storing metal alloy of this invention was covered with nickel like the publication to JP,60-190570,A, it became clear that the oxidation resistance of an alloy is improved. However, although this technique is effective in oxidation-resistant improvement, since the nickel itself which covered the alloy front face does not almost have hydrogen-absorption capacity, the amount of hydrogen absorption per alloy unit weight falls. Then, since this nickel addition layer has bigger hydrogen-absorption capacity than pure nickel by changing into nickel addition layer which nickel enveloping layer on the front face of an alloy is made to react with the Ti-V-Cr alloy used as a base material as a result of inquiring further, and makes a Ti-nickel compound a subject, it turns out that oxidation resistance can be given to a hydrogen storing metal alloy, without reducing most amounts of hydrogen absorption. Therefore, in the suitable mode, the hydrogen storing metal alloy of this invention has nickel addition layer which makes a Ti-nickel compound a subject on the alloy front face.
[0046] The covering method of nickel on the front face of an alloy is a physical method. (the method equivalent to the mechanical alloying mixed with an example, the method of mixing nickel impalpable powder and the end of an alloy powder, a ball mill, etc. is also included) Chemical method (an example, electrolysis nickel plating, non-

electrolyzed nickel plating) Any are sufficient and there is especially no limit. Although the amount of covering of nickel changes also with mean particle diameters of the powder of a hydrogen storing metal alloy, 5 - 10 % of the weight is usually preferably suitable for it one to 20% of the weight to a hydrogen storing metal alloy. As long as it is required before this nickel covering, pickling processing of the hydrogen storing metal alloy may be carried out from the acid of non-oxidizing qualities, such as fluoric acid and a hydrochloric acid, and the oxidizing zone on the front face of an alloy may be removed.

[0047] After covering the front face of a hydrogen storing metal alloy with nickel, nickel addition layer which makes a Ti-nickel compound a subject is formed in a front face by heat-treating, making Ti component in a base material alloy nickel in surface coating react, and changing nickel layer to the high Ti-nickel compound of hydrogen-absorption capacity. Since this nickel addition layer has incorporated Cr from the base material, it excels the 2 yuan system intermetallic compound of Ti-nickel in oxidation resistance.

[0048] It is desirable to also perform this heat treatment in a vacuum or inert gas in order to prevent oxidization of an alloy. Heat treatment conditions are set up so that it will not change big and rough, by the time the diameter of average crystal grain of the main phase of a base material alloy exceeds 40 micrometers during this heat treatment. This viewpoint to heat treatment temperature It considers as the range of 400 - 750 **. If heat treatment temperature exceeds 750 **, big and rough-ization of the sludge of the 2nd phase progresses, and the amount of hydrogen absorption will fall or it will become easy to carry out pulverization of the diameter of average crystal grain to hydrogen absorption and discharge by the repeat. On the other hand, the generation reaction of a Ti-nickel compound cannot progress easily under by 400 **. Desirable heat treatment temperature It is 450-600 **.

[0049] However, it is a long time for example, in a ball mill about nickel covering. (an example and 100 - 1000 hours) Since it is nickel addition layer which generated nickel covering already reacts with Ti in a base material alloy, and makes a Ti-nickel compound a subject when it carries out by the method equivalent to the mechanical alloying of carrying out, it is not necessary to heat-treat for a reaction.

[0050]

[Example] In production of an examination alloy, it is the RF dissolution. (5 kg/ch) Button arc dissolution (button size : 250 g/ch and 50 g/ch) Single roll quenching which used the copper roll (20 g/ch) Ar gas atomization (10 g/ch) Rotational electrode process (500 g/ch) It used. The raw materials used for manufacture of an alloy molten metal were titanium sponge of 99 % of the weight of purity, vanadium of 98 % of the weight of purity, and chromium of 99 % of the weight of purity.

[0051] They are 300 ** and 2.5 MPa about the alloy obtained by methods other than the gas atomization from which powder is obtained directly, and a rotating electrode. After hydrogenating in hydrogen gas for 5 hours, it ground mechanically, and it was made powder. Any end of an alloy powder is 100. The powder below mum was sorted out and used with the sieve. About a part of gas atomization material, in order to enlarge the diameter of average crystal grain, it heat-treated in argon atmosphere. The characterization method of an examination alloy is explained below collectively.

[0052] Hydrogen gas absorption, emission characteristic hydrogen gas absorption, and the emission characteristic were measured using G BERUTSU type equipment. Measurement is 200 ** and 2.5 MPa first about an examination alloy. After leaving it for 12 hours and carrying out activation into hydrogen gas, the dehydrogenation treatment was performed by 300 **, and it carried out by making hydrogen absorb at 80 degrees C. In order to remove the influence of oxidization of a front face in the end of an alloy powder in machine pulverization, pickling of the examination alloy was carried out in 5vol% fluoric acid solution before activation. The amount of hydrogen absorption is 0.5MPa(s) of the discharge curve of 1 cycle eye. H/M which is the ratio of the metal atomic number which measures hydrogen storage capacity and constitutes an alloy, and the absorbed number of hydrogen atoms A value estimates and it is H/M. 1.5 The above was considered as success.

[0053] The influence of the pulverization by pulverization repeat hydrogen absorption and discharge measured and evaluated whether only in which, powder with a particle size of 20 micrometers or less increased the measurement examination of the aforementioned hydrogen absorption and emission characteristic after 300 cycle ******. The particle-size-distribution measuring device of a laser diffraction formula was used for the particle size analysis. Since the difference was in powdered particle size distribution by the manufacture method, evaluation computed the fines rate of increase compared to the amount on the basis of the particle weight 20 micrometers or less before an examination by the following formula, and evaluated it. It is success if the fines rate of increase is 15% or less.

[0054]

[Equation 1]

$$微粉増加率(\%) = \left[\frac{A-B}{B}\right] \times 100$$

A=300 サイクル試験後の20 μ m以下の粉末量、
B=試験前の20 μ m以下の粉末量。

[0055] After measurement of the diameter of crystal grain of the main phase of the diameter examination alloy of crystal grain embedded the alloy before pulverization at the epoxy resin and ground it, it **********ed by the mixed acid of 0.4 vol% fluoric acid and a 1vol% nitric acid, was observed with the optical microscope, and it was performed, and the average of the measurement result of 20 crystal grain chosen at random was made into the diameter of average crystal grain. Since it was detailed, the particle size of the sludge of the 2nd phase is SEM (secondary electron microscope). It used and measured and the average was calculated like the top.

[0056] Oxidation-resistant evaluation of the hydrogen storing metal alloy which carried out nickel covering of the oxidation-resistant front face, and formed nickel addition layer, the constant temperature of the temperature of 25 degrees C, and 65% of humidity -- G BERUTSU [after leaving it for one week in the air atmosphere of constant humidity] type hydrogen absorption / discharge testing device -- using -- activation -- nothing -- 70 degrees C -- 2.5 MPa The absorption test of hydrogen gas was performed and the decreasing rate of the amount of hydrogen absorption in comparison with the hydrogen amount of adsorption of the alloy before forming nickel addition layer was computed by the following formula. It is success if the amount decreasing rate of hydrogen absorption is 10% or less.

[0057]

[Equation 2]

$$水素吸収量低下率(\%) = \left[\frac{C-D}{C}\right] \times 100$$

C=Ni被覆前に活性化処理して測定した水素吸収量
D=1週間放置後に70℃で測定した水素吸収量

[0058] (Example 1) this example is an example which alloy composition was changed and examined the performance of a hydrogen storing metal alloy. Only the rapid solidification method was adopted as a method of producing a hydrogen storing metal alloy. The diameter of average crystal grain of the main phase, the amount of hydrogen absorption, and the measurement result of the fines rate of increase are shown in Table 1.

[0059]

[Table 1]

合金No.	化学組成			作製方法	平均結晶粒径 (μm)	水素吸収量 (H/M)	微増加率 (%)	備考
	Ti	V	Cr					
1	0.50	0.40	0.10	ガスアトマイズ	17	1.61	5	本発明例
2	0.50	0.08	0.42	ガスアトマイズ	16	1.70	12	
3	0.30	0.60	0.10	ガスアトマイズ	22	1.54	3	
4	0.30	0.28	0.42	ガスアトマイズ	21	1.75	8	
5	0.40	0.30	0.30	ガスアトマイズ	18	1.77	7	
6	0.40	0.40	0.20	ガスアトマイズ	20	1.65	6	
7	0.30	0.30	0.40	ロール急冷	15	1.74	9	
8	0.30	0.30	0.40	回転電極	17	1.75	8	
9	0.50	<u>0.00</u>	<u>0.50</u>	ガスアトマイズ	24	1.62	25*	比較例
10	<u>0.60</u>	0.10	0.40	ガスアトマイズ	15	1.35*	10	
11	<u>0.60</u>	0.30	0.10	ガスアトマイズ	16	1.27*	8	
12	0.30	0.20	<u>0.50</u>	ガスアトマイズ	18	1.38*	16*	
13	<u>0.20</u>	0.60	0.20	ガスアトマイズ	22	1.20*	5	

(注) 下線部の数値：本発明の範囲外
* 不合格

[0060] Each hydrogen storing metal alloy of the example of this invention whose alloy composition is this invention within the limits as shown in Table 1 is H/M. 1.5 A high amount of hydrogen absorption called the above and 15% or less of low rate of pulverization are combined, and it turns out that there are many amounts of hydrogen

absorption, and there is little degradation by repeat hydrogen absorption and discharge.
[0061] On the other hand, with the alloy of the example of comparison of No.9 which have much Ti and Cr and do not have V addition, although the amount of hydrogen absorption is large, it is very a pulverization plain-gauze cone. With the alloy of the example of comparison of No.8-11 with which Ti and the amount of Cr(s) separated from this invention range, although pulverization is quiet, it has few amounts of hydrogen absorption.
[0062] (Example 2) this example is an example which considered the influence the diameter of average crystal grain of the main phase of the hydrogen storing metal alloy produced by the various manufacture methods affects the performance of a hydrogen storing metal alloy. The chemical composition of an alloy was taken as the same composition of Ti=0.40, V= 0.30, and Cr=0.30. In order to see the influence of the diameter of crystal grain, the examination alloy heat-treated after gas atomization was also produced. A test result is shown in Table 2. [0063]
[Table 2]

合金No.	溶解方法	主相の平均結晶粒径 (μm)	析出物の結晶粒径 (μm)	水素吸収量 (H/M)	微粉増加率 (%)	備考
1	ガスアトマイズ	18	0.5	1.77	7	本発明例
2	ロール急冷	19	0.5	1.76	9	
3	回転電極	15	0.4	1.78	7	
4	ガスアトマイズ 熱処理: 680 ℃×10hr	32	1.5	1.72	13	
5	ボタンアーク溶解, 50g	<u>50</u>	3.5	1.65	21*	比較例
6	ボタンアーク溶解, 250g	<u>70</u>	7.1	1.55	25*	
7	高周波溶解, 5kg	<u>85</u>	6.0	1.45*	32*	
8	ガスアトマイズ 熱処理: 900 ℃×15hr	<u>55</u>	2.2	1.58	18*	
9	ガスアトマイズ 熱処理: 1300℃×10hr	<u>65</u>	3.5	1.43*	25*	

(注) 下線部の数値：本発明の範囲外
* 不合格

[0064] If a hydrogen storing metal alloy is produced by the rapid solidification method as shown in Table 2, the alloy of the organization where the diameter of average crystal grain of the main phase is as detailed as about 20 micrometers or less will be obtained. Although the diameter of crystal grain became big and rough when the hydrogen storing metal alloy of this detailed organization was heat-treated, when the diameter of average crystal grain of the main phase was 40 micrometers or less, both the amount of hydrogen absorption and the fines rate of increase were success. However, the examination alloy which especially the diameter of average crystal grain has not heat-treated after rapid solidification 20 micrometers or less showed the property in which the fines rate of increase was excellent with 10% or less.
[0065] In addition, the desirable range of the suppression of pulverization especially of [that the diameter of average crystal grain of the main phase is 40 micrometers or less] 2 micrometers or less understands a bird clapper also for 5 micrometers or less also of diameters of average crystal grain of the sludge of the 2nd phase from Table 2.
[0066] On the other hand, although button arc dissolution material had comparatively many amounts of hydrogen absorption, the fines rate of increase became large. (5 No. 6) . In RF dissolution material, both the amount of hydrogen absorption and the fines rate of increase became a rejection. (No.7) . When gas atomization material was heat-treated and heat treatment conditions were set up so that the diameter of average crystal grain might exceed 40 micrometers, the fines rate of increase became a rejection, and when big-and-rough-izing of the diameter of crystal grain was excessive, the amount of hydrogen absorption also fell greatly.
[0067] (Example 3) this example illustrates the oxidation-resistant improvement in the hydrogen storing metal alloy at the time of forming in an alloy front face nickel addition layer which makes a Ti-nickel compound a subject. Each examined hydrogen storing metal alloy is the powder produced by the Ar gas atomizing method. The chemical composition of an alloy was taken as the same composition of Ti=0.40, V= 0.30, and Cr=0.30 except for one example. (let this be Alloy A) . The one remaining examples (alloy B) It was Ti=0.30, V= 0.60, and Cr=0.10. In order to see the influence of the diameter of crystal grain, the examination alloy heat-treated after gas atomization was also produced.
[0068] nickel covering of the hydrogen storing metal alloy powder for forming nickel addition layer adopted both

the physical method and the chemical method. By the physical method, after blending this 10% of the weight to the end of an alloy powder using nickel impalpable powder with a particle size of about 1 micrometer, it mixed uniformly with the mortar or mixed with the ball mill for a long time. The chemical method formed about 10% of the weight of nickel plating layer in the front face in the end of an alloy powder using commercial non-electrolyzed nickel plating liquid. In addition, though natural, even if it performs electrolysis plating, same nickel plating layer can be formed.

[0069] After giving nickel covering by these methods, nickel addition layer which makes a Ti-nickel compound a subject was formed in the alloy front face by heat-treating in argon atmosphere, making nickel enveloping layer react with the end of an alloy powder, and alloying. However, with the method of covering nickel powder with a ball mill mechanically, it is this ball mill mixture 100 Since alloying of nickel covering by mechanical alloying had taken place by carrying out time and for a long time, heat treatment was not performed. Moreover, as an example of comparison, this heat treatment was not performed but the test coupon which only carried out nickel covering was also produced.

[0070] In this way, the oxidation resistance of the hydrogen storing metal alloy powder produced by the gas atomizing method for having formed nickel content layer on the front face was investigated after the neglect for one week in the atmosphere of predetermined conditions as mentioned above. About a test result, it is the formation method of nickel addition layer. (an upper case is the nickel covering method and the lower berth is heat treatment conditions) Existence of formation of the diameter of average crystal grain of the main phase, and a Ti-nickel compound phase (it checks with X diffraction equipment) It is shown in Table 3.

[0071]

[Table 3]

合金No	化学組成 1)	Ni含有層形成法 上：Ni被覆法 下：熱処理条件	平均結晶粒径 (μm)	Ni付加層形成の有無	水素吸収量低下率 (%)	備考
1	A	無電解めっき 680℃×10hr	22	有	6	本発明例
2	A	Ni粉末乳鉢混合 680℃×10hr	22	有	9	
3	A	Ni粉末ボールミル混合 100 hr	18	有	9	
4	A	無電解めっき 400℃×25hr	20	有	7	
5	B	無電解めっき 680℃×10hr	24	有	7	
6	A	Ni被覆なし	18	—	30*	比較例
7	A	無電解めっき 熱処理なし	18	無	23*	
8	A	Ni粉末乳鉢混合 熱処理なし	18	無	26*	
9	A	無電解めっき 900℃×10hr	51	有	17*	

(注) 1) A：Ti=0.40, V=0.30, Cr=0.30
B：Ti=0.30, V=0.60, Cr=0.10
* 不合格

[0072] As shown in Table 3, nickel covering was given according to this invention, when nickel addition layer which makes a Ti-nickel compound a subject by making nickel covering of a parenthesis react with an alloy content was formed in the alloy front face, oxidization in the atmosphere of the hydrogen storing metal alloy of this invention was suppressed, and the fall of the amount of hydrogen absorption was suppressed also for after one-week neglect to 10% or less. Consequently, the handling in the alloy-powder end of the inside of the atmosphere becomes simple, and reactivation processing when a front face oxidizes becomes unnecessary.

[0073] On the other hand, in the example of comparison, when nickel covering was not given at all, the amount of hydrogen absorption of the alloy-powder end after one-week neglect fell no less than 30%. (examination No.5) . However, even if it gave nickel covering, when nickel covering was not made to react with an alloy content by heat treatment or mechanical alloying, the amount of hydrogen absorption of the alloy-powder end after one-week neglect fell no less than 23 to 26%. (examination No.6, 7) . That is, compared with the case of not covering, it turns out only by nickel covering that there is almost no oxidation-resistant improvement. Moreover, when the heat

treatment temperature after nickel covering was too high and the diameter of average crystal grain of the main phase exceeded 40 micrometers, the amount of hydrogen absorption fell greatly under the influence of big-and-rough-izing.

[0074]

[Effect of the Invention] the hydrogen storing metal alloy of this invention -- the amount of hydrogen absorption -- many -- comparatively low temperature near the room temperature (an example and below 150 **) since it is hard to carry out pulverization even if it is easy to use for various uses and repeats hydrogen absorption and discharge over a long period of time, since absorption and discharge of hydrogen take place, the high amount of hydrogen absorption holds for a long period of time -- having -- (namely, -- long lasting) And it is comparatively cheap.

[0075] moreover, the base in the case of the oxidation resistance of an alloy improving remarkably and using it into the atmosphere, if nickel addition layer which makes a Ti-nickel compound a subject is formed in an alloy front face -- since the fall of the amount of absorption becomes very small, it becomes possible to deal with it easily in the atmosphere, and reactivation processing becomes unnecessary The hydrogen storing metal alloy of this invention is the the best for hydrogen storage and transportation, a heat transport, a cooling system, and a hydrogen gas refining use.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention is the amount of hydrogen absorption. (hydrogen-absorption capacity) Highly and simultaneous, repeatedly, it is few, and property degradation by hydrogen absorption discharge can use at the temperature near the room temperature, and is related with a hydrogen storing metal alloy with the feature of being comparatively cheap, and its manufacture method. The hydrogen storing metal alloy of this invention with the above-mentioned feature is the the best for the object for hydrogen gas storage, and hydrogen gas refining.

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PRIOR ART

[Description of the Prior Art] Hydrogen gas is an energy source cleaner than the fossil fuel of the former [form / neither carbon dioxide gas nor nitrogen oxide / at the time of combustion]. Although the high-pressure hydrogen gas container was used in many cases on the occasion of its storage and transportation, since liquefaction temperature of hydrogen gas was low, it had to use the large-sized bomb for saving a lot of hydrogen gas, and had the fault that the storage container volume and weight became large.
[0003] As for a hydrogen storing metal alloy, since the absorption discharge of the hydrogen gas can be carried out in reversible, if the hydrogen storing metal alloy which can carry out occlusion of a lot of hydrogen gas is used for storage and transportation of hydrogen, since it will become more nearly lightweight than the bomb which can store a lot of hydrogen by high density, and stores the hydrogen of this capacity rather than a bomb, transportation also has easily the advantage that it is strong also against a mechanical shock. Therefore, research and development of the hydrogen storing metal alloy aiming at hydrogen storage and transportation have been done conventionally.
[0004] Since absorption of the hydrogen by the hydrogen storing metal alloy is the hydrogenation reaction of an alloy and discharge of hydrogen is the decomposition reaction of a hydride, at the time of absorption of hydrogen gas, and discharge, generation of heat and an endothermic are produced, respectively. This property is used and they are a heat-transport system, and warming or a cooling system about a hydrogen storing metal alloy. (an example, heat pump) Using is also possible.
[0005] The hydrogen absorption discharge speed of a hydrogen storing metal alloy is larger than the rate of absorption of other gas constituents, and since there is a difference also by hydrogen and its isotope, a hydrogen storing metal alloy can also be used for the use which refines hydrogen gas out of the gas containing impure gas constituents using the difference in such a hydrogen-absorption property.
[0006] For the above-mentioned use, a hydrogen storing metal alloy will all repeat and receive absorption and discharge of hydrogen gas while in use. In order to obtain a practical reaction rate in absorption and discharge of this hydrogen gas, it is necessary to powder-ize a hydrogen storing metal alloy and to increase a surface area. A predetermined container is filled up with this powdered hydrogen storing metal alloy, and use is presented.
[0007] In case a hydrogen storing metal alloy absorbs and emits hydrogen gas, in addition to the above-mentioned generation of heat and endothermic, expansion and contraction of about 10 - 20% of volume also take place. Therefore, if absorption and discharge of hydrogen gas are repeated and received while in use, a crack will go into the powder of a hydrogen storing metal alloy, and the pulverization which a powder particle is destroyed and becomes an impalpable powder will happen. If this pulverization advances, fines will be got blocked within a container and the problem that hydrogen gas will not flow easily or fines move into gas piping by the flow of hydrogen gas will arise. The pulverization suppression in the end of an alloy powder in repeat use poses a very big problem from such a situation in utilization of a hydrogen storing metal alloy.
[0008] An alloy cannot prevent touching with the atmosphere at the time of production of the hydrogen-absorption equipment using the hydrogen storing metal alloy. If a hydrogen storing metal alloy touches and oxidizes to the atmosphere, since an oxide film will generate on an alloy front face and the oxide film will serve as an obstacle of hydrogen absorption, hydrogen storage capacity falls. Especially as for V alloy, it is tended to check oxidization hydrogen absorption. In order to enable it to use V alloy which oxidized at once, a hydrogen bomb which is equal to such processing is not only expensive, but it must heat a hydrogen storing metal alloy to an elevated temperature in high-pressure hydrogen, and size and weight increase are not avoided. Then, the oxidation-resistant improvement of a hydrogen storing metal alloy is also a practically important problem.
[0009] Thus, although there is a broad use in a hydrogen storing metal alloy, even when using for what use, the amount of hydrogen absorption is the most important property. Moreover, depending on a use, it is the comparatively low temperature near the room temperature. (an example and below 150 **) It is also important that

absorption and discharge of hydrogen take place. Furthermore, the price of an alloy is also very important practically for the use which uses a hydrogen storing metal alloy in large quantities.
[0010] For example, $LaNi_5$ which utilization preceded most Or $MmNi_5$ AB_5 represented It is expensive, and even if the amount of the hydrogen storing metal alloy used can use the hydrogen storing metal alloy of type for few small rechargeable batteries, it is difficult to use it for the use which needs a lot of hydrogen storing metal alloys called the object for hydrogen storage.
[0011] To JP,59-38293,B, it is comparatively cheap, and the Ti-Cr-V system hydrogen storing metal alloy is indicated as a high capacity hydrogen storing metal alloy. As the manufacture method of an alloy, only the arc process is explained concretely. The hydrogen storing metal alloy which consists of the same components also as JP,7-252560,A is indicated. The analogous hydrogen storing metal alloy of a Ti-V-nickel system is indicated by JP,7-268513,A and JP,7-268514,A.
[0012] Moreover, it is explained to JP,60-190570,A that influence of contamination by the impurity gas in atmosphere can be made small by covering copper and/or a nickel metal with wet electroless deposition to hydrogen storing metal alloy powder.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] the hydrogen storing metal alloy of this invention -- the amount of hydrogen absorption -- many -- comparatively low temperature near the room temperature (an example and below 150 **) since it is hard to carry out pulverization even if it is easy to use for various uses and repeats hydrogen absorption and discharge over a long period of time, since absorption and discharge of hydrogen take place, the high amount of hydrogen absorption holds for a long period of time -- having -- (namely, -- long lasting) And it is comparatively cheap.
[0075] moreover, the base in the case of the oxidation resistance of an alloy improving remarkably and using it into the atmosphere, if nickel addition layer which makes a Ti-nickel compound a subject is formed in an alloy front face -- since the fall of the amount of absorption becomes very small, it becomes possible to deal with it easily in the atmosphere, and reactivation processing becomes unnecessary The hydrogen storing metal alloy of this invention is the the best for hydrogen storage and transportation, a heat transport, a cooling system, and a hydrogen gas refining use.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] It has been experienced that they are not right in fact although a theory top should have many amounts of hydrogen absorption and the Ti-Cr-V system hydrogen storing metal alloy and Ti-V-nickel system alloy which were mentioned above must be excellent in hydrogen-absorption capacity. This is considered that a cause is for 2nd phase called TiCr2 with few amounts of hydrogen absorption to generate, therefore for hydrogen-absorption capacity decline by such alloy system.

[0014] For example, when it manufactures by the arc process as indicated by this official report, since solidification speed is slow, a Ti-Cr-V system hydrogen storing metal alloy given in JP,59-38293,B is low TiCr2 of hydrogen storage capacity as the 2nd phase sludge. An intermetallic compound generates at a remarkable rate and hydrogen storage capacity declines. Moreover, a crack enters with this 2nd phase as the starting point into the repeat of hydrogen absorption and discharge in the end of an alloy powder, and there is also a trouble that pulverization is promoted.

[0015] In the example of JP,7-252560,A, in order to reduce the 2nd above-mentioned phase, after holding at the elevated temperature of 1200-1400 degrees C and considering as a cubic single phase organization, the process which quenches with water cooling immediately is taken. However, since big and rough-ization of crystal grain arises in the case of heating-at-high-temperature maintenance, even if the amount of sludges of the 2nd phase decreases, the intensity of the material itself becomes weak by big and rough-ization, and it on the contrary becomes easy to carry out pulverization of it by such method. In case it moreover mass-produces industrially, in order to use a large-sized ingot, even if it carries out water cooling after heating, sufficient cooling rate will not be obtained, but a big and rough sludge will be formed, and hydrogen storage capacity will also decline.

[0016] A Ti-nickel intermetallic compound is characterized by forming a 3-dimensional mesh frame at a grain boundary into the host phase which a Ti-V-nickel system hydrogen storing metal alloy given in each official report of JP,7-268513,A and said 268514 numbers becomes from a Ti-V system solid-solution alloy. Since such a grain-boundary phase raises reactivity with the hydrogen of an alloy, even if a mother layer has some oxidization, hydrogen gas absorption discharge is possible through this grain-boundary phase. However, since many 2nd phase to the extent that the 3-dimensional network structure is taken is formed, the hydrogen quantity to be stored of the whole alloy falls by the low 2nd phase formation of hydrogen-absorption capacity, and there is a trouble that the pulverization on the basis of this 2nd phase arises.

[0017] Moreover, since there is no hydrogen-absorption capacity in this covering itself when Cu or nickel metal is covered on the surface of a hydrogen storing metal alloy like a publication to JP,60-190570,A, only in the part of covering, the amount of hydrogen absorption will decrease.

[0018] Even if this invention has repeat hydrogen absorption / discharge life high hydrogen-absorption capacity applicable to storage and transportation of hydrogen, a heat transport, a cooling system, hydrogen gas refining, etc., and over a long period of time, and it can be used for it at the temperature near the room temperature and it keeps it in the atmosphere, it makes a technical problem the thing with little hydrogen-absorption property degradation for which a comparatively cheap hydrogen storing metal alloy is offered.

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MEANS

[Means for Solving the Problem] This invention persons have high hydrogen-absorption capacity and outstanding repeat hydrogen absorption / discharge life, and are low temperature (150 degrees C or less) near the room temperature comparatively. As a result of doing research on the hydrogen storing metal alloy which can be used, when the Ti-Cr-V system hydrogen storing metal alloy was manufactured by the rapid solidification method and the diameter of crystal grain was made small, it found out that the above-mentioned technical problem was solvable, and this invention was reached.

[0020] this invention is Tia V1-a-bCrb here. It is expressed with a formula and the value of a The value of 0.3-0.5b It is the hydrogen storing metal alloy which has the chemical composition which are 0.1-0.45, and is characterized by the diameter of average crystal grain of the main phase being 40 micrometers or less.

[0021] This hydrogen storing metal alloy is Tia V1-a-bCrb. It is expressed with a formula and the value of a The value of 0.3 to 0.5 and b It can manufacture by ingoting the alloy which has the chemical composition which are 0.1-0.45 by the rapid solidification method.

[0022] In the suitable mode of this invention, it has nickel addition layer to which a hydrogen storing metal alloy makes a Ti-nickel compound a subject on a front face. the front face of a hydrogen storing metal alloy which manufactured this nickel addition layer by ** rapid solidification method -- nickel covering -- carrying out -- subsequently -- or it heat-treats at the temperature of 400 - 750 ** -- or ** -- it can form by carrying out nickel covering of the front face of this hydrogen storing metal alloy by the mechanical alloying method

[0023]

[Embodiments of the Invention] Hereafter, this invention is explained in detail. The feature of the hydrogen storing metal alloy of this invention is **Tia V1-a-bCrb. Chemical composition shown (the inside of a formula, a:0.3-0.5, b:0.1-0.45) The diameters of average crystal grain of the ** main phase are 40 micrometers or less and two points of being detailed.

[0024] The main phase of this hydrogen storing metal alloy is a dissolution body whorl which consists of three elements of Ti, V, and Cr, and a crystalline form is a body center cubic. The diameter of average crystal grain of the detailed main phase of the above-mentioned ** can attain a hydrogen storing metal alloy by manufacturing by rapid solidification methods, such as a chill roll method and the gas atomizing method. For example, if the cooling rate at the time of solidification becomes slow like an arc solution process, since crystal grain will grow and it will become big and rough during solidification, the diameter of average crystal grain of the main phase will exceed 40 micrometers.

[0025] The Ti-V-Cr system hydrogen storing metal alloy of this invention which fulfills the conditions of above ** and ** is the low TiCr2 of hydrogen-absorption capacity. Since there are few amounts of deposits of the 2nd said phase, the temperature requirement below 150 ** is also 0.1 MPa near the atmospheric pressure. Absorbing very many hydrogen gas, the hydrogen absorbed dose is H/M. Ratio (a number of a hydrogen atom of ratios absorbed to one metal atom which constitutes an alloy) 1.5 It increases with the above. Moreover, 0.1 MPa It is endurance that for below 150 ** and a low reason use near the room temperature below 150 ** is possible for the temperature which shows balanced hydrogen pressure, and it cannot receive pulverization easily. (life) It becomes the hydrogen storing metal alloy which was very excellent. Moreover, since the rare earth metal is not included, the raw material cost of an alloy is not so high, either.

[0026] The crystalline form of the sludge of the 2nd above-mentioned phase is hexagonal or a cubic, and this exists in the interior of the grain-boundary section of a body center cubic which is the main phase of the hydrogen storing metal alloy of this invention, or a grain. First, the reason which limited the chemical composition of the hydrogen storing metal alloy of this invention like ** is explained. In addition, as shown in the formula of the above-mentioned chemical composition, each amount of each element is an atomic ratio, and the sum total is set to 1.

[0027] (Titanium Ti): If the amount of Ti increases, the grid size of the alloy main phase of a body center cubic will be expanded, and the hydrogen absorbed dose will increase. H/M 1.2 It is 0.3 in order to obtain the above high hydrogen absorbed dose. If the above Ti is required and the amount of Ti is less than this, the hydrogen absorbed dose will become low. If many titanium is added too much, although the hydrogen absorbed dose will increase further, hydrogen equilibrium pressure falls too much and it becomes impossible to use near a room temperature and the atmospheric pressure.

[0028] Therefore, although Cr is added as an element which raises hydrogen equilibrium pressure, the amount of Ti is 0.5. Endurance over the pulverization by the repeat of hydrogen absorption and discharge when hydrogen equilibrium pressure cannot be raised to near the atmospheric pressure even if it adds Cr, if it exceeds (alloy life) It gets worse. addition of Ti from a viewpoint of balance with the hydrogen absorbed dose and an alloy life the range of 0.3-0.45 -- desirable -- more -- desirable -- 0.3-0.4 It is within the limits.

[0029] Chromium (Cr): If Cr addition increases, although the hydrogen absorbed dose increases, it is not so large as titanium the extent. The key objective of Cr addition is in control of hydrogen equilibrium pressure. Therefore, the addition changes with the service temperatures and hydrogen equilibrium pressure which are made into Ti addition and the purpose. Cr is 0.1. In the case of Ti0.3, the hydrogen equilibrium pressure in a room temperature becomes below atmospheric pressure, and it is no longer made to absorb and emit hydrogen in reversible at a room temperature at the following. TiCr2 which deposits as the 2nd phase on the other hand if Cr exceeds 0.45 Not only the hydrogen absorbed dose falls, but the amount of a phase increases and the life over repeat hydrogen absorption and discharge falls. the addition of Cr -- from a viewpoint of the balance of the hydrogen absorbed dose and an alloy life within the limits of 0.2-0.45 -- desirable -- more -- desirable -- 0.3-0.4 it is .

[0030] (Vanadium V): With the 2 yuan system alloy of Ti-Cr, it is TiCr2 as the 2nd phase. It forms mostly and the hydrogen absorbed dose and an alloy life fall, and since hydrogen equilibrium pressure is also too low and use at a room temperature is difficult for it, V is added. Many body center cubic phases are obtained by addition of V, and the hydrogen absorbed dose increases. The addition of V is automatically determined by the addition of Ti and Cr.

[0031] If the hydrogen absorbed dose of this alloy changes with the diameters of average crystal grain of the manufacture method or the main phase, the cooling rate at the time of solidification becomes slow and the diameter of average crystal grain of the main phase exceeds 40 micrometers even if it has the chemical composition of the Ti-Cr-V ternary system explained above, even if it is the same chemical composition, the hydrogen absorbed dose will fall. This is TiCr2 when solidification speed falls. Since this sludge has little hydrogen absorbed dose of itself, when the rate in which a sludge [like] is formed as the 2nd phase increases, and the 2nd phase of the amount of formation increases, the hydrogen absorbed dose as the whole alloy is for falling.

[0032] If the rate in which this sludge is formed as the 2nd phase increases, since Ti in the alloy phase of a body center cubic which is the main phase, and the amount of Cr(s) will fall, it originates mainly in the amount reduction of Cr(s), the hydrogen equilibrium pressure which is balanced gas ** of hydrogen absorption and release reaction falls the hydrogen absorbed dose of the main phase not only decreases, but, and it becomes impossible moreover, to emit the hydrogen absorbed in reversible.

[0033] In addition, it also sets to the hydrogen storing metal alloy of this invention which fills both the above-mentioned ** and **, and is TiCr2. Although it is not avoided that a sludge [like] deposits as the 2nd phase, since there are few the amounts, these troubles are canceled substantially.

[0034] Furthermore, the hydrogen storing metal alloy of this invention is pulverization to which expansion and contraction of the alloy volume by the repeat of absorption and discharge of hydrogen take place owing to. (it can judge by the fall of a powder mean particle diameter) It is hard to receive and excels in endurance very much. This outstanding endurance is MmNi5 known as a rare earth system hydrogen storing metal alloy. It is more remarkably [than a system intermetallic compound] good.

[0035] However, if it changes with the diameters of average crystal grain of the manufacture method or the main phase, the cooling rate at the time of solidification becomes slow like [the endurance over this pulverization] the hydrogen absorbed dose and the diameter of average crystal grain of the main phase exceeds 40 micrometers, pulverization will become easy to happen even if it is the same chemical composition. TiCr2 which is the 2nd phase when a cooling rate becomes slow in this way, as mentioned above Since the amount of generation increases, pulverization is presumed that the intergranular fracture on the basis of this 2nd phase is the main factor.

[0036] From the above knowledge, the diameter of average crystal grain of the main phase is limited to 40 micrometers or less by the hydrogen storing metal alloy of this invention. Endurance over pulverization (alloy life) In order to improve further, it is desirable that the diameter of average crystal grain of the main phase is 20 micrometers. Moreover, it is hard coming to generate after ******** in 5 micrometers or less, and if the diameter of average crystal grain of the sludge formed as the 2nd phase is 2 micrometers or less, it will hardly carry out

pulverization.
[0037] The hydrogen storing metal alloy of this invention whose diameter of average crystal grain of the main phase is 40 micrometers or less can be manufactured by ingoting the alloy molten metal of predetermined composition by the rapid solidification method. As long as the hydrogen storing metal alloy of this invention with the diameter of average crystal grain of the above [a rapid solidification method] is obtained, there is no limit. Generally, a cooling rate is 103 **/sec. What is necessary is just the solidifying method which becomes the above.
[0038] As a rapid solidification method employable by this invention, it is the method of carrying out teeming of the alloy molten metal on a rotational electrode process, a rotating drum, or a roll. (an example, a single roll, or congruence chill roll method) A method, the gas atomizing method, etc. which are thinly cast to up to a water-cooled copper plate are mentioned. A rotational electrode process and the atomizing method have [among these] a powder configuration advantageous at the point that pack density becomes high in a globular form substantially, when the trituration process for being able to manufacture the spherical-powder end of a hydrogen storing metal alloy, and carrying out the pulverization becomes unnecessary. In the case of other methods, the hydrogen storing metal alloy obtained if needed is ground, and it is made powder. As the trituration method, both hydrogenation trituration and machine trituration can be adopted and both may be used together.
[0039] It is appropriate for the hydrogen storing metal alloy of this invention to consider as the powder gestalt whose mean particle diameter is about 10-50 micrometers. Thereby, a surface area increases and absorption and release reaction of hydrogen are promoted. If required, a classification will adjust a mean particle diameter.
[0040] The hydrogen storing metal alloy of this invention manufactured by the rapid solidification method has a minute quenching distortion. This quenching distortion is the endurance of the hydrogen storing metal alloy of this invention. (pulverization) Although not generated, especially a remarkable bad influence may heat-treat a hydrogen storing metal alloy by request, and may remove this quenching distortion. As for this heat treatment, it is desirable to carry out in a vacuum or inert gas in order to prevent oxidization of an alloy.
[0041] It is necessary to set up heat treatment conditions so that there may be no bird clapper during heat treatment more greatly [the diameter of average crystal grain of the alloy main phase] than 40 micrometers. This condition is usually temperature, although it changes also with diameters of average crystal grain of the main phase of the hydrogen storing metal alloy manufactured by the rapid solidification method. It is within the limits of 400-750 degree-Cx 2 - 20 hours.
[0042] However, since it may heat-treat by the morphosis of this layer and quenching distortion is also removed during this heat treatment when forming in an alloy front face nickel addition layer which makes a Ti-nickel compound a subject in order to raise the oxidation resistance of the hydrogen storing metal alloy of this invention so that it may mention later, heat treatment of only the purpose of removal of the quenching distortion in that case is unnecessary. It is not desirable from a viewpoint of big-and-rough-izing of the diameter of average crystal grain to perform two heat treatments to the hydrogen storing metal alloy of this invention.
[0043] The hydrogen storing metal alloy of this invention is the low temperature near a room temperature, when it is left in the atmosphere. (an example, 70 degrees C) The measured hydrogen absorbed dose decreases. This alloy that carried out air neglect is also among high-pressure hydrogen gas. (20 atmospheric pressure) If it is made to heat and reactivate to 500 **, the hydrogen absorbed dose will increase and the absorbed dose before neglect will be recovered. That is, if this alloy is left in the atmosphere, a front face will oxidize, and this oxide film is considered that it becomes an obstacle and the hydrogen storage capacity in low temperature decreases.
[0044] In order that it may not be avoided for the use of the object for storage or the object for refining of hydrogen gas that a hydrogen storing metal alloy is **(ed) by the atmosphere and operating temperature may avoid the fall of below 150 ** and the hydrogen absorbed dose by the above-mentioned oxidization since it is low temperature comparatively, it is desirable to improve the oxidation resistance of the hydrogen storing metal alloy of this invention.
[0045] As a result of examining this point, when the front face of the hydrogen storing metal alloy of this invention was covered with nickel like the publication to JP,60-190570,A, it became clear that the oxidation resistance of an alloy is improved. However, although this technique is effective in oxidation-resistant improvement, since the nickel itself which covered the alloy front face does not almost have hydrogen-absorption capacity, the hydrogen absorbed dose per alloy unit weight falls. Then, since this nickel addition layer has bigger hydrogen-absorption capacity than pure nickel by changing into nickel addition layer which nickel enveloping layer on the front face of an alloy is made to react with the Ti-V-Cr alloy used as a base material as a result of inquiring further, and makes a Ti-nickel compound a subject, it turns out that oxidation resistance can be given to a hydrogen storing metal alloy, without reducing most hydrogen absorbed dose. Therefore, in the suitable mode, the hydrogen storing metal alloy of this invention has nickel addition layer which makes a Ti-nickel compound a subject on the alloy front face.

[0046] The covering method of nickel on the front face of an alloy is a physical method. (the method equivalent to the mechanical alloying mixed with an example, the method of mixing nickel impalpable powder and the end of an alloy powder, a ball mill, etc. is also included) Chemical method (an example, electrolysis nickel plating, non-electrolyzed nickel plating) Any are sufficient and there is especially no limit. Although the amount of covering of nickel changes also with mean particle diameters of the powder of a hydrogen storing metal alloy, 5 - 10 % of the weight is usually preferably suitable for it one to 20% of the weight to a hydrogen storing metal alloy. As long as it is required before this nickel covering, pickling processing of the hydrogen storing metal alloy may be carried out from the acid of non-oxidizing qualities, such as fluoric acid and a hydrochloric acid, and the oxidizing zone on the front face of an alloy may be removed.
[0047] After covering the front face of a hydrogen storing metal alloy with nickel, nickel addition layer which makes a Ti-nickel compound a subject is formed in a front face by heat-treating, making Ti component in a base material alloy nickel in surface coating react, and changing nickel layer to the high Ti-nickel compound of hydrogen-absorption capacity. Since this nickel addition layer has incorporated Cr from the base material, it excels the 2 yuan system intermetallic compound of Ti-nickel in oxidation resistance.
[0048] It is desirable to also perform this heat treatment in a vacuum or inert gas in order to prevent oxidization of an alloy. Heat treatment conditions are set up so that it will not change big and rough, by the time the diameter of average crystal grain of the main phase of a base material alloy exceeds 40 micrometers during this heat treatment. This viewpoint to heat treatment temperature It considers as the range of 400 - 750 **. If heat treatment temperature exceeds 750 **, big and rough-ization of the sludge of the 2nd phase progresses, and the hydrogen absorbed dose will fall or it will become easy to carry out pulverization of the diameter of average crystal grain to hydrogen absorption and discharge by the repeat. On the other hand, the generation reaction of a Ti-nickel compound cannot progress easily under by 400 **. Desirable heat treatment temperature It is 450-600 **.
[0049] However, it is a long time for example, in a ball mill about nickel covering. (an example and 100 - 1000 hours) Since it is nickel addition layer which generated nickel covering already reacts with Ti in a base material alloy, and makes a Ti-nickel compound a subject when it carries out by the method equivalent to the mechanical alloying of carrying out, it is not necessary to heat-treat for a reaction.

[Translation done.]

EXAMPLE

[Example] In production of an examination alloy, it is the RF dissolution. (5 kg/ch) Button arc dissolution (button size : 250 g/ch and 50 g/ch) Single roll quenching which used the copper roll (20 g/ch) Ar gas atomization (10 g/ch) Rotational electrode process (500 g/ch) It used. The raw materials used for manufacture of an alloy molten metal were titanium sponge of 99 % of the weight of purity, vanadium of 98 % of the weight of purity, and chromium of 99 % of the weight of purity.

[0051] They are 300 ** and 2.5 MPa about the alloy obtained by methods other than the gas atomization from which powder is obtained directly, and a rotating electrode. After hydrogenating in hydrogen gas for 5 hours, it ground mechanically, and it was made powder. Any end of an alloy powder is 100. The powder below mum was sorted out and used with the sieve. About a part of gas atomization material, in order to enlarge the diameter of average crystal grain, it heat-treated in argon atmosphere. The characterization method of an examination alloy is explained below collectively.

[0052] Hydrogen gas absorption, emission characteristic hydrogen gas absorption, and the emission characteristic were measured using G BERUTSU type equipment. Measurement is 200 ** and 2.5 MPa first about an examination alloy. After leaving it for 12 hours and carrying out activation into hydrogen gas, the dehydrogenation treatment was performed by 300 **, and it carried out by making hydrogen absorb at 80 degrees C. In order to remove the influence of oxidization of a front face in the end of an alloy powder in machine trituration, pickling of the examination alloy was carried out in 5vol% fluoric acid solution before activation. The hydrogen absorbed dose is 0.5MPa(s) of the discharge curve of 1 cycle eye. H/M which is the ratio of the metal atomic number which measures hydrogen storage capacity and constitutes an alloy, and the absorbed number of hydrogen atoms A value estimates and it is H/M. 1.5 The above was considered as success.

[0053] The influence of the pulverization by pulverization repeat hydrogen absorption and discharge is the measurement examination of the aforementioned hydrogen absorption and emission characteristic 300 It measured and evaluated which powder with a particle size of 20 micrometers or less increased after cycle ******. The particle-size-distribution measuring device of a laser diffraction formula was used for the particle size analysis. Since the difference was in powdered particle size distribution by the manufacture method, evaluation computed the fines rate of increase compared to the amount on the basis of the particle weight 20 micrometers or less before an examination by the following formula, and evaluated it. It is success if the fines rate of increase is 15% or less.

[0054]

[Equation 1]

$$\text{微粉増加率(\%)} = \left[\frac{A-B}{B}\right] \times 100$$

A＝300 サイクル試験後の20μm以下の粉末量.
B＝試験前の20μm以下の粉末量。

[0055] After measurement of the diameter of crystal grain of the main phase of the diameter examination alloy of crystal grain embedded the alloy before trituration at the epoxy resin and ground it, it **********ed by the mixed acid of 0.4 vol% fluoric acid and a 1vol% nitric acid, was observed with the optical microscope, and it was performed, and the average of the measurement result of 20 crystal grain chosen at random was made into the diameter of average crystal grain. Since it was detailed, the particle size of the sludge of the 2nd phase is SEM (secondary electron microscope). It used and measured and the average was calculated like the top.

[0056] Oxidation-resistant evaluation of the hydrogen storing metal alloy which carried out nickel covering of the oxidation-resistant front face, and formed nickel addition layer, the constant temperature of the temperature of 25 degrees C, and 65% of humidity -- G BERUTSU [after leaving it for one week in the air atmosphere of constant

humidity] type hydrogen absorption / discharge testing device -- using -- activation -- nothing -- 70 degrees C -- 2.5 MPa The absorption test of hydrogen gas was performed and the decreasing rate of the hydrogen absorbed dose in comparison with the hydrogen amount of adsorption of the alloy before forming nickel addition layer was computed by the following formula. It is success if a hydrogen absorbed-dose decreasing rate is 10% or less.

[0057]

[Equation 2]

$$\text{水素吸収量低下率(\%)} = \left[\frac{C-D}{C}\right] \times 100$$

C=Ni被覆前に活性化処理して測定した水素吸収量
D=1週間放置後に70℃で測定した水素吸収量

[0058] (Example 1) this example is an example which alloy composition was changed and examined the performance of a hydrogen storing metal alloy. Only the rapid solidification method was adopted as a method of producing a hydrogen storing metal alloy. The diameter of average crystal grain of the main phase, the hydrogen absorbed dose, and the measurement result of the fines rate of increase are shown in Table 1.

[0059]

[Table 1]

合金No.	化学組成 Ti	V	Cr	作製方法	平均結晶粒径 (μm)	水素吸収量 (H/M)	微増加率 (%)	備考
1	0.50	0.40	0.10	ガスアトマイズ	17	1.61	5	本発明例
2	0.50	0.08	0.42	ガスアトマイズ	16	1.70	12	
3	0.30	0.60	0.10	ガスアトマイズ	22	1.54	3	
4	0.30	0.28	0.42	ガスアトマイズ	21	1.75	8	
5	0.40	0.30	0.30	ガスアトマイズ	18	1.77	7	
6	0.40	0.40	0.20	ガスアトマイズ	20	1.65	6	
7	0.30	0.30	0.40	ロール急冷	15	1.74	9	
8	0.30	0.30	0.40	回転電極	17	1.75	8	
9	0.50	0.00	0.50	ガスアトマイズ	24	1.62	25*	比較例
10	0.60	0.10	0.40	ガスアトマイズ	15	1.35*	10	
11	0.60	0.30	0.10	ガスアトマイズ	16	1.27*	8	
12	0.30	0.20	0.50	ガスアトマイズ	18	1.38*	16*	
13	0.20	0.60	0.20	ガスアトマイズ	22	1.20*	5	

(注) 下線部の数値：本発明の範囲外
* 不合格

[0060] Each hydrogen storing metal alloy of the example of this invention whose alloy composition is this invention within the limits as shown in Table 1 is H/M. 1.5 High hydrogen absorbed dose called the above and 15% or less of rate of low pulverization are combined, and it turns out that there is much hydrogen absorbed dose and there is little degradation by repeat hydrogen absorption and discharge.

[0061] On the other hand, with the alloy of the example of comparison of No.9 which have much Ti and Cr and do not have V addition, although the hydrogen absorbed dose is large, it is very a pulverization plain-gauze cone. With the alloy of the example of comparison of No.8-11 with which Ti and the amount of Cr(s) separated from this invention range, although pulverization is quiet, it has little hydrogen absorbed dose.

[0062] (Example 2) this example is an example which considered the influence the diameter of average crystal grain of the main phase of the hydrogen storing metal alloy produced by the various manufacture methods affects the performance of a hydrogen storing metal alloy. The chemical composition of an alloy was taken as the same composition of Ti=0.40, V= 0.30, and Cr=0.30. In order to see the influence of the diameter of crystal grain, the examination alloy heat-treated after gas atomization was also produced. A test result is shown in Table 2. [0063]

[Table 2]

合金No.	溶解方法	主相の平均結晶粒径 (μm)	析出物の結晶粒径 (μm)	水素吸収量 (H/M)	微粉増加率 (%)	備考
1	ガスアトマイズ	18	0.5	1.77	7	本発明例
2	ロール急冷	19	0.5	1.76	9	
3	回転電極	15	0.4	1.78	7	
4	ガスアトマイズ 熱処理: 680 ℃×10hr	32	1.5	1.72	13	
5	ボタンアーク溶解, 50g	50	3.5	1.65	21*	比較例
6	ボタンアーク溶解, 250g	70	7.1	1.55	25*	
7	高周波溶解, 5kg	85	6.0	1.45*	32*	
8	ガスアトマイズ 熱処理: 900 ℃×15hr	55	2.2	1.58	18*	
9	ガスアトマイズ 熱処理: 1300℃×10hr	65	3.5	1.43*	25*	

(注) 下線部の数値：本発明の範囲外
* 不合格

[0064] If a hydrogen storing metal alloy is produced by the rapid solidification method as shown in Table 2, the alloy of the organization where the diameter of average crystal grain of the main phase is as detailed as about 20 micrometers or less will be obtained. Although the diameter of crystal grain became big and rough when the hydrogen storing metal alloy of this detailed organization was heat-treated, when the diameter of average crystal grain of the main phase was 40 micrometers or less, both the hydrogen absorbed dose and the fines rate of increase were success. However, the examination alloy which especially the diameter of average crystal grain has not heat-treated after rapid solidification 20 micrometers or less showed the property in which the fines rate of increase was excellent with 10% or less.
[0065] In addition, the desirable range of the suppression of pulverization especially of [that the diameter of average crystal grain of the main phase is 40 micrometers or less] 2 micrometers or less understands a bird clapper also for 5 micrometers or less also of diameters of average crystal grain of the sludge of the 2nd phase from Table 2.
[0066] On the other hand, although button arc dissolution material had comparatively much hydrogen absorbed dose, the fines rate of increase became large. (5 No. 6) . In RF dissolution material, both the hydrogen absorbed dose and the fines rate of increase became a rejection. (No.7) . When gas atomization material was heat-treated and heat treatment conditions were set up so that the diameter of average crystal grain might exceed 40 micrometers, the fines rate of increase became a rejection, and when big-and-rough-izing of the diameter of crystal grain was excessive, the hydrogen absorbed dose also fell greatly.
[0067] (Example 3) this example illustrates the oxidation-resistant improvement in the hydrogen storing metal alloy at the time of forming in an alloy front face nickel addition layer which makes a Ti-nickel compound a subject. Each examined hydrogen storing metal alloy is the powder produced by the Ar gas atomizing method. The chemical composition of an alloy was taken as the same composition of Ti=0.40, V= 0.30, and Cr=0.30 except for one example. (let this be Alloy A) . The one remaining examples (alloy B) It was Ti=0.30, V= 0.60, and Cr=0.10. In order to see the influence of the diameter of crystal grain, the examination alloy heat-treated after gas atomization was also produced.
[0068] nickel covering of the hydrogen storing metal alloy powder for forming nickel addition layer adopted both the physical method and the chemical method. By the physical method, after blending this 10% of the weight to the end of an alloy powder using nickel impalpable powder with a particle size of about 1 micrometer, it mixed uniformly with the mortar or mixed with the ball mill for a long time. The chemical method formed about 10% of the weight of nickel plating layer in the front face in the end of an alloy powder using commercial non-electrolyzed nickel plating liquid. In addition, though natural, even if it performs electrolysis plating, same nickel plating layer can be formed.
[0069] After giving nickel covering by these methods, nickel addition layer which makes a Ti-nickel compound a subject was formed in the alloy front face by heat-treating in argon atmosphere, making nickel enveloping layer react with the end of an alloy powder, and alloying. However, with the method of covering nickel powder with a ball mill mechanically, it is this ball mill mixture 100 Since alloying of nickel covering by mechanical alloying had taken place by carrying out time and for a long time, heat treatment was not performed. Moreover, as an example of

comparison, this heat treatment was not performed but the test coupon which only carried out nickel covering was also produced.

[0070] In this way, the oxidation resistance of the hydrogen storing metal alloy powder produced by the gas atomizing method for having formed nickel content layer on the front face was investigated after the neglect for one week in the atmosphere of predetermined conditions as mentioned above. About a test result, it is the formation method of nickel addition layer. (an upper case is the nickel covering method and the lower berth is heat treatment conditions) Existence of formation of the diameter of average crystal grain of the main phase, and a Ti-nickel compound phase (it checks with X diffraction equipment) It is shown in Table 3.

[0071]

[Table 3]

合金No.	化学組成 1)	Ni含有層形成法 上：Ni被覆法 下：熱処理条件	平均結晶粒径 (μm)	Ni付加層形成の有無	水素吸収量低下率 (%)	備考
1	A	無電解めっき 680℃×10hr	22	有	6	本発明例
2	A	Ni粉末乳鉢混合 680℃×10hr	22	有	9	
3	A	Ni粉末ボールミル 混合 100 hr	18	有	9	
4	A	無電解めっき 400℃×25hr	20	有	7	
5	B	無電解めっき 680℃×10hr	24	有	7	
6	A	Ni被覆なし	18	—	30*	比較例
7	A	無電解めっき 熱処理なし	18	無	23*	
8	A	Ni粉末乳鉢混合 熱処理なし	18	無	26*	
9	A	無電解めっき 900℃×10hr	<u>51</u>	有	17*	

(注) 1) A : Ti=0.40, V=0.30, Cr=0.30
B : Ti=0.30, V=0.60, Cr=0.10
* 不合格

[0072] As shown in Table 3, nickel covering was given according to this invention, when nickel addition layer which makes a Ti-nickel compound a subject by making nickel covering of a parenthesis react with an alloy content was formed in the alloy front face, oxidization in the atmosphere of the hydrogen storing metal alloy of this invention was suppressed, and the fall of the hydrogen absorbed dose was suppressed also for after one-week neglect to 10% or less. Consequently, the handling in the alloy-powder end of the inside of the atmosphere becomes simple, and reactivation processing when a front face oxidizes becomes unnecessary.

[0073] On the other hand, in the example of comparison, when nickel covering was not given at all, the hydrogen absorbed dose of the alloy-powder end after one-week neglect fell no less than 30%. (examination No.5). However, even if it gave nickel covering, when nickel covering was not made to react with an alloy content by heat treatment or mechanical alloying, the hydrogen absorbed dose of the alloy-powder end after one-week neglect fell no less than 23 to 26%. (examination No.6, 7). That is, compared with the case of not covering, it turns out only by nickel covering that there is almost no oxidation-resistant improvement. Moreover, when the heat treatment temperature after nickel covering was too high and the diameter of average crystal grain of the main phase exceeded 40 micrometers, the hydrogen absorbed dose fell greatly under the influence of big-and-rough-izing.

[Translation done.]